CHAPTER 7

CLASS D FIRE SUPPRESSION EXPERIMENTS

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CLASS D FIRE SUPPRESSION EXPERIMENTS

7.1   Objective

To investigate the effectiveness of water based extinguishing agents on non alkali Class D fires, two series of fire suppression experiments were conducted. The first experimental series was conducted by Underwriters Laboratory at the facility located in Northbrook, Illinois. It consisted of magnesium chip fire tests as outlined in the Standard for Rating and Fire Testing of Fire Extinguishers, ANSI/UL 711 [1]. The second series of experiments, conducted by The Building and Fire Research Laboratory were performed at the University of Maryland Fire Rescue Institute training facility located in Princess Anne County, Maryland. This second series utilized titanium turnings as the fuel for the experiments.

7.2 Background

A Class D fire is defined as a fire in a combustible metal, such as magnesium, titanium, zirconium, sodium, lithium, or potassium [2]. In the proper environment, all metals except gold, silver, and platinum will burn [3] and perhaps the most important condition which regulates the combustibility of a metal is its form and shape [4]. In this respect, metals are no different than many other combustible solids. Some metals that are difficult to ignite in a large solid form, will ignite and burn readily as thin sheets, shavings, or particles. Additionally, many metals in the form of a powder or dust will ignite explosively. Several metal dusts, among them aluminum, magnesium, thorium, titanium, and uranium have explosibility indexes greater than 10 which is considered severe [5]. Some of these metals can produce maximum rates of pressure rise in excess of 68.95 MPa/s (10,000 psi/s).

The extinguishment of metal fires is difficult since many burning metals react violently with most of the common extinguishing agents used today. The reactivity of some metals, such as aluminum, magnesium, and zirconium, is so high that they continue to burn even in the presence of nitrogen forming their nitrides [6]. In addition, metals burn at very high temperatures, up to 4500 °C (8100 °F) [3]. In the combustion of ordinary hydrocarbons, the flame temperature is limited by dissociation of CO_2. This begins to become appreciable at temperatures about 1400 °C (2550 °F) and effectively limits hydrocarbon flame temperatures to less than 2200 °C (4000 °F) [7]. At 2500 °C (4500 °F) water is dissociated into hydrogen and hydroxide [8]. When water is applied to these burning metals, the hydrogen produced by this dissociation increases the combustion and explosion hazard. Dry chemicals, based on bicarbonates are also ineffective against metal fires since these metals react with the carbon dioxide, which is a decomposition product of bicarbonates. Some metals will burn in an atmosphere of carbon dioxide. Compounds containing halogen react violently with some burning metals. The use of halogen containing suppressant agents on pure metal fires is considered hazardous [9]. The use of a halogenated extinguishing agent, such as halon 1301, on magnesium or titanium, may evolve more heat than could be obtained from reaction with oxygen. Thus the suppressant could become an accelerant [10]. The alkali metals, lithium, sodium, potassium, rubidium, and cesium, react with water with an explosive violence. The melting point

of the alkali metals are relatively low, ranging from 28°C to 180°C (83 °F to 356 °F). In contact with water these metals have an exothermic reaction which raises the temperature causing the metal to melt increasing the surface area for reaction. These metals may ignite spontaneously when exposed to the atmosphere. Alkali metals also react exothermically with the halogens. Therefore, halogenated hydrocarbons cannot be used to extinguish alkali metal fires. The reaction of alkali metals with halogenated hydrocarbons is nearly as violent as their reaction with water.

Over the years a great deal of effort has been expended in the study of different agents for the extinguishment of combustible metal fires [11,12,13]. Hundreds of agents have been tested in many different experimental scenarios. They include dry chemicals, dry powders, gases, and liquids, including water based extinguishing agents. Many different standard test fires were considered along with different requirements for what was considered a successful extinguishing agent. Many agents tested were considered highly toxic. Extinguishment of visible flame was not always considered the sole requirement for an extinguishing agent, since metals sometimes continued to burn under a coating of agent until completely consumed. Control, rather than extinguishment was often the goal. Other requirements included a reduction in temperature of the burning metal, or a requirement of a specific percentage of the metal that would be salvageable after a test fire. Often, an agent was tested at various concentrations and flow rates on a specific combustible metal. Numerous agents have been developed to extinguish combustible metal fires, but a given agent does not necessarily control or extinguish all metal fires. Although some agents are valuable in working with several metals, other agents are useful in extinguishing only one type of metal. Additionally, some agents provide only partial control and cannot be classed as an actual extinguishing agent. An additional problem related with the use of some extinguishing agents is the amount needed to control or extinguish a metal fire. Many times the amount of extinguishing agent needed greatly exceeds the amount of metal that is burning. Presently, Underwriters Laboratory test Class D fire extinguishers, or an extinguishing agent arranged for manual handling, on a given combustible metal. Unlike Class A and Class B extinguishers there are no numerical components for Class D ratings. Extinguishing agents for use on Class D fires are rated for the amount of agent and the method of application needed to control a fire involving a particular quantity and type of metal. The type of combustible metal for which the extinguisher or agent is applicable and the area, depth, and other characteristics of the fire which may be controlled or extinguished are as stated in published literature from the manufacturer and as described in the manufacturer's recommendations for use. An example of an Underwriters Laboratories listing for a specific extinguishing agent states that the ratio of extinguishing agent to metal is 5 to 1 when used on a magnesium fire and 15 to 1 when the same agent is used on a molten sodium potassium alloy fire.
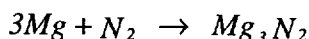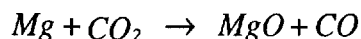
7.3   Magnesium

Fires in magnesium and magnesium alloys, similar to other combustible metals, present severe extinguishing problems in that the great reactivity of magnesium precludes the use of common fire extinguishing agents. Magnesium has such a strong affinity for oxygen that it extracts the oxygen from oxygen containing compounds [14]. Magnesium reacts with water to form hydrogen and magnesium hydroxide in such a manner that the combustion of the magnesium is accelerated, and the hydrogen burns, supplying increased fuel to the fire. This reaction is expressed by the following

equation:

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$$
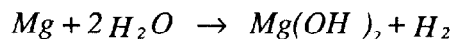
Because ordinary water based foam agents contain more than 90% water, they are ineffective in extinguishing burning magnesium. In a confined space, magnesium will continue to burn in air after the available oxygen has been used by combining with nitrogen to form magnesium nitride. In an inert atmosphere of carbon dioxide, magnesium will react to produce magnesium oxide and carbon monoxide. These reactions are described as follows:

$$Mg + CO_2 \rightarrow MgO + CO$$

$$3Mg + N_2 \rightarrow Mg_3N_2$$

The National Fire Protection Association (NFPA) Fire Protection Handbook, 17th edition [15], indicates that water may be used to extinguish magnesium fires if it can be applied rapidly and in large enough quantities to have a cooling effect. Small streams from portable extinguishers will accelerate a magnesium chip fire violently. Well advanced fires in several hundred pounds of magnesium scrap have been extinguished in less than 1 minute using two 38 mm (1½ in) fire hoses [15]. The total quantity or application rate of the water is not indicated. Tests conducted by the Chicago Fire Department showed that the use of large quantities of water may cool magnesium below its ignition temperature and so control the fire [16]. Two tests are described. Both consisted of burning magnesium in a shed with the dimensions of 3.04 x 3.04 x 3.04 m. (10 x 10 x 10 ft). Sprinklers installed in the shed consisted of six open heads with orifices of 8 mm (5/16 in). The first test with 40 kg (72½ lbs) of magnesium fines, chips, and solids in the form of castings was ignited and allowed to burn for 15 minutes before water was applied through the sprinklers. Although the amount of water flow was not described in the text, the sprinklers were supplied at an initial pressure of 861 kPa (125 psi) for the first 5 minutes, 1034 kPa (150 psi) for five minutes and then 1379 kPa (200 psi) for five minutes. There was a momentary flare up or intensification of burning upon application of water. After this 15 minute application, the water was shut off due to the appearance of the fire being extinguished. The remaining magnesium was stirred in an effort to check for complete extinguishment. It re-ignited spontaneously. Water was again applied for an additional eight minutes before the magnesium was finally extinguished. The second test consisted of 95 kg (210 lbs) of magnesium fines and solids. The magnesium was ignited and allowed to burn for 12 minutes before water was applied through the sprinklers. For this test, the sprinklers were replaced by standard heads with 12.7 mm (½ in) orifices. After 8 minutes of water application through the sprinklers, three 63.5 mm (2 ½ inch) hose lines equipped with 28.6 mm (1 1/8 inch) tips supplied at a pressure of 1206 kPa (175 psi) were used to extinguish the fire. As with the first test there was

a momentary flare up upon water application and additional mild flashes and explosive reactions upon water application from the hoses. As can be seen from the number of sprinklers, hoses and the supply pressures, copious amounts of water were needed to control and extinguish these magnesium fires. One of the hoses, if supplied at a standard pressure of 345 kPa (50 psi) [17,18] would supply 1000 l/min (265 g/min). Therefore the three hoses alone supplied almost 3000 l/min (800 g/min) of water or a density of 325 l/min/m^2 (8 g/min/ft^2).

The National Fire Protection Association Standard 480, Storage, Handling, and Processing of Magnesium Solids and Powders, 1993 Edition [19] recommends against the use of water as an extinguishing agent. This standard does not permit the use of automatic sprinklers in areas where molten magnesium is produced or handled, in areas where heat treating furnaces are located, or in areas where magnesium chips or powders are produced or handled. It strictly prohibits the use of automatic sprinklers in buildings where magnesium powder may be stored and only allows the use of sprinklers in buildings used to store heavy or light magnesium castings if other ordinary combustible materials are present. NFPA Standard 49 Hazardous Chemical Data, 1994 Edition [20] advises not to use carbon dioxide, halogenated extinguishing agents, water or foam on magnesium fire. The method of extinguishing magnesium fires depends largely on the form of the material. The National Fire Protection Association Fire Protection Handbook, 17th edition recommends that burning chips, shavings, and small parts be extinguished by smothering and cooling with a suitable dry extinguishment agent. Where magnesium dust is present care must be taken not to cause a dust cloud from forming during agent application, as this may result in a dust explosion. If surrounding materials can be removed and the amount of magnesium is small, it may be best to let the magnesium burn itself out.

In two recent incidents involving large amounts of magnesium on fire, water was never considered as an extinguishing agent [21,22]. The first involved approximately 2270 kg (5000 lbs) of magnesium scrap in the form of hollow tubes of 3.8 cm (1 ½ inch) diameter and rectangular poles 5 cm x 10 cm x 3.7 m (2 in x 4 in x 12 ft). This fire was extinguished with the use 1140 kg (2500 lbs) of soda ash. The second fire involving approximately 4100 kg (9000 lbs) of magnesium chips and turnings was extinguished with the use of approximately 10500 kg (23000 lbs) of sand.

7.4 Titanium

Titanium also has an extremely high affinity for oxygen and nitrogen. Additionally the oxides of titanium are readily soluble in the molten metal. Thus, heated titanium can not only easily reduce many of the compounds or liquids normally used as extinguishing agents, and the absence of a protective oxide film results in the presence of a continuously reactive surface on the molten metal [12]. Although water has been used successfully in some cases, in others, violent reactions were reported. [12, 15]. The National Fire Protection Association Fire Protection Handbook, 17th edition, indicates that water may not be used on titanium powder, but can be used with caution in other titanium fires. Hose streams have been used effectively on fires outside piles of scrap, but violent reactions resulting in serious injuries have been reported in other cases where water was applied to hot or burning titanium. Tests on titanium machining and in open drums showed that a coarse water spray was effective in relative small quantities of material. Neither the amount of burning titanium

involved, the amount of water used, nor the application rate of the water was indicated. The National Fire Protection Association Standard 481, Production, Processing, Handling, and Storage of Titanium, 1995 Edition [23] recommends against the use of water-based extinguishers as extinguishing agents. Buildings or portions of buildings of non combustible construction used principally for titanium storage or handling shall not be permitted to be equipped with automatic sprinkler protection unless combustibles other than titanium create a more severe hazard than the titanium. Carbon dioxide also reacts with titanium. The equilibrium reaction of equal masses of titanium and carbon dioxide results in carbon monoxide, titanium oxide and titanium dioxide at a temperature of 3099 °C (5600 °F), well above its ignition temperature. Extinguishment tests using carbon dioxide on titanium fires showed that a 23% concentration of carbon dioxide increased the burning rate by 50%, while tests with nearly 100% carbon dioxide showed an increase in the burning rate of about 300% [24]. Nitrogen also encouraged the combustion of bulk titanium in air, rather than suppressing it. Reaction of either liquid or gaseous nitrogen with titanium will produce temperatures of 3200 °C (5800 °F).

7.5   Experiments

The experiments conducted by Underwriters Laboratories Inc. were done as outlined in the Standard for Rating and Fire Testing of Fire Extinguishers, ANSI/UL 711. The Underwriters Laboratories report is attached in its entirety in Appendix E. The Underwriters Laboratories tested four biodegradable, environmentally safe, nontoxic, liquid fire suppression agents; water; and an Underwriters Laboratories listed Class D dry powder agent on a magnesium chip fire (Figures 1 and 2). The magnesium chip fire consisted of 9 or 18 kg (20 or 40 lbs) of dry grignard magnesium grade chips arranged in a 61 cm x 61 cm (2 ft x 2 ft) area on a 6 mm (1/4 in) steel plate. The grignard chips were approximately 6 to 9 mm (1/4 to 3/8 in) long, 3 mm (1/8 in) wide, and 2 mm (1/10 in) thick. The grignard chips were ignited using a hand torch along one side and allowed to burn undisturbed until a deep seated condition was observed such that approximately 50 percent of the magnesium was consumed. Following this freeburn period, suppression began with the extinguishing agents. For the tests involving the Underwriters Laboratories Class D dry powder, a nominal 14 kg (30 lb) dry powder extinguisher was used to apply the agent. The dry powder was applied from a distance of approximately 1.5 m (5 ft) from the fire and for a duration of approximately 35 seconds. For the tests involving the liquid agents or water, a single adjustable pattern discharge nozzle was used to discharge the liquid agents or water at a flow rate of 38 l/min (10 g/min). The nozzle was adjusted to a straight stream pattern and fitted with an air aspirating attachment for one series of fire tests and used as a spray nozzle without the air aspirating attachment for a send series of tests. The liquid agents or water were applied from a distance of approximately 4.5 m (15 ft) from the fire and for a duration of 5 minutes. During each fire test, observations were made for fire extinguishment, reaction of the applied agent with the magnesium, approximate amount of magnesium consumed, and fire spread.

The experiments conducted by the Building and Fire Research Laboratory consisted of 9 kg (20 lbs) piles of oiled titanium turnings arranged in a 61 x 61 x 15 cm high pile (2 ft x 2 ft x 6 in) placed on a 6 mm (1/4 in) steel plate. The steel plate was placed inside a 2.14 m (84 in) diameter steel containment pan. The steel plate was supported on cinder blocks so that the steel plate was at the

same level as the rim of the pan. The titanium was ignited using a MAPP gas burner along one side of the pile and allowed to burn undisturbed until a deep seated burning condition was observed such that the flame front had traveled approximately half of the distance across the pile. Following this free burn period, suppression began with the extinguishing agents. For all the tests, the extinguishing agent was applied with a hand held nozzle a distance of approximately 1 m (3 ft) from the fire. During agent application, observations were made for fire extinguishment and reaction of the applied agent with the titanium.

Base line tests were conducted with water to identify a lower limit of application that would not immediately suppress the fire. These baseline tests started at an application rate of 37 l/min (10 g/min), which was the flow used in the magnesium test fires. Unlike the magnesium test fires, this flow rate easily extinguished the titanium fires. The base line experiments indicated a flow rate of 3.7 l/min (1 g/min) of water did not always extinguish the fire. This flow rate was used for all extinguishing agents.

7.6 Results and Discussion

The results of the magnesium chip fire tests presented in Table 1. The results indicate that the biodegradable, environmentally safe, non toxic, liquid fire suppression agents were unable to extinguish a Class D combustible metal fire involving magnesium chips. The spray application method offered some advantage over the stream application method by providing a gentler application of agent onto the fire. This gentler application also resulted in smaller quantities of burning magnesium being scattered beyond the test bed area. When the magnesium material was scattered beyond the test bed area, it continued to burn intensely and had the potential to ignite other combustibles. The tests conducted with the Underwriters Laboratories Listed Class D dry powder agent resulted in complete extinguishment of the test fires and no scattering of burning magnesium beyond the test bed area.

Results for the titanium fire experiments are presented in Tables 2. The results of the titanium fire tests show 7 of the 11 tests using water based extinguishing agents successfully extinguished the test fire. All the fire tests using water or water based extinguishing agent initially increased the intensity of the fire. This increase in intensity lasted approximately 10 to 50 seconds after initial application. After this initial increase in intensity, the flame height of the fire and intensity appeared to return to the burning level before agent application. With continued agent application, 7 of the 11 test fires were extinguished within 2 minutes of the start of agent application. In test number 21 a Class D extinguishing agent was used. This particular agent was not listed for use on titanium fires. Although this agent did not completely extinguish the fire it greatly reduced the burning intensity of the fire and was the only agent used that did not cause an initial increase in the fire intensity upon application. Although all the water based extinguishing agents initially increased the intensity of the fire, none appeared to have caused the level of sparking or fuel scattering as seen in the magnesium fire tests.

7.7 Conclusions

When tested on magnesium fires the water based extinguishing agents performed similarly to water. Water failed to extinguish the fire and caused the fire to increase in intensity and spread beyond the area of origin. All four of the water based extinguishing agents did the same. When tested on the titanium fires, results were again similar to water. Water alone extinguished one of the two titanium test fires. The water based extinguishing agents extinguished 6 of the 9 titanium test fires. In all cases the water and water based extinguishing agents increased the intensity of the fire upon initial application. However neither water nor the water based extinguishing caused the fire to spread beyond the area of origin as they did in the magnesium test fires. This may have been due to the very slow application rate of the agent in the titanium test fires compared to the application rate in the magnesium test fires. In both series of tests there did not appear to be any benefit gained by using the water based extinguishing agent over that of water.

The Underwriter's Laboratory ANSI/UL 711, Standard for Rating and Fire Testing of Fire Extinguishers test scenario appears to be an acceptable test method for testing Class D extinguishing agents on a small scale. However if fire departments are to use these extinguishing agents on large fires as is shown in references 21 and 22, then a large scale test method should be developed. Several attempts at developing large scale tests have been attempted in the past [25,26]. These test methods often used quantities of burning metals in the hundreds of kg [lbs] range.

7.8 References

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Table 1 - Magnesium Chip Fire Test Results

Test Number	Pounds of Magnesium	Extinguishing Agent	Preburn Min:Sec	Method of Application	Rate of Application	Duration of Application Min:Sec	Visual Adverse Reaction	Increased Intensity of Fire	Fire Spread Beyond Steel Plate	Fire Extinguished
1	20	Class D Powder	15:00	Direct	na	0:32	None	No	No	Yes
2	40	Class D Powder	25:00	Direct	na	0:34	None	No	No	Yes
3	20	Water	25:00	Stream	10 GPM	5:00	Sparking	Substantial	Yes	No
4	20	Water	25:00	Spray	10 GPM	5:00	Sparking	Moderate	Yes	No
5	20	Liquid-A 1%	25:00	Stream	10 GPM	5:00	Sparking	Substantial	Yes	No
6	20	Liquid-A 1%	25:00	Spray	10 GPM	5:00	Sparking	Moderate	Yes	No
7	20	Liquid-B 1%	25:00	Stream	10 GPM	5:00	Sparking	Substantial	Yes	No
8	20	Liquid-B 1%	25:00	Spray	10 GPM	5:00	Sparking	Moderate	Yes	No
9	20	Liquid-C 1%	25:00	Stream	10 GPM	5:00	Sparking	Substantial	Yes	No
10	20	Liquid-C 1%	25:00	Spray	10 GPM	5:00	Sparking	Moderate	Yes	No
11	20	Liquid-D 1%	25:00	Stream	10 GPM	5:00	Sparking	Substantial	Yes	No

Table 2 - Titanium Turnings Fire Test Results

| Test Number	Pounds of Titanium	Extinguishing Agent	Preburn Min:Sec	Method	Rate of Application	Duration of Application Min:Sec	Visual Adverse Reaction	Fire Spread Beyond Steel Plate	Increased Intensity of Fire	Fire Extinguished
10	20	Water	2:55	Stream	1 GPM	2:00	None	No	Yes	No
11	20	Water	2:20	Stream	1 GPM	2:00	None	No	Yes	Yes
12	20	1% Agent A	4:08	Stream	1 GPM	2:00	None	No	Yes	Yes
13	20	1% Agent A	5:55	Stream	1 GPM	2:25	None	No	Yes	Yes
14	20	1% Agent B	3:00	Stream	1 GPM	2:00	None	No	Yes	Yes
15	20	1% Agent B	3:30	Spray	1 GPM	2:00	None	No	Yes	Yes
16	20	6% Agent C	3:02	Stream	1 GPM	2:00	None	No	Yes	Yes
17	20	6% Agent C	1:30	Spray	1 GPM	2:00	None	No	Yes	No
18	20	6% Agent C	2:00	Spray	1 GPM	2:00	None	No	Yes	No
19	20	3% Agent D	2:00	Stream	1 GPM	2:00	None	No	Yes	No
20	20	3% Agent D	2:23	Spray	1 GPM	2:00	None	No	Yes	Yes
21	20	Class D	21:45	Direct	na	0:23	None	No	No	No
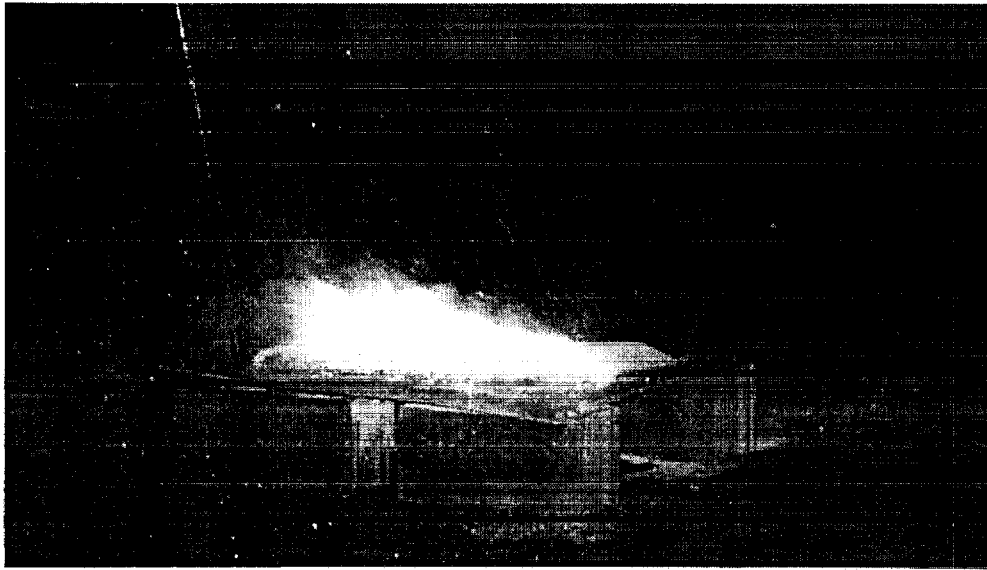
Figure 1. Magnesium fire before suppression
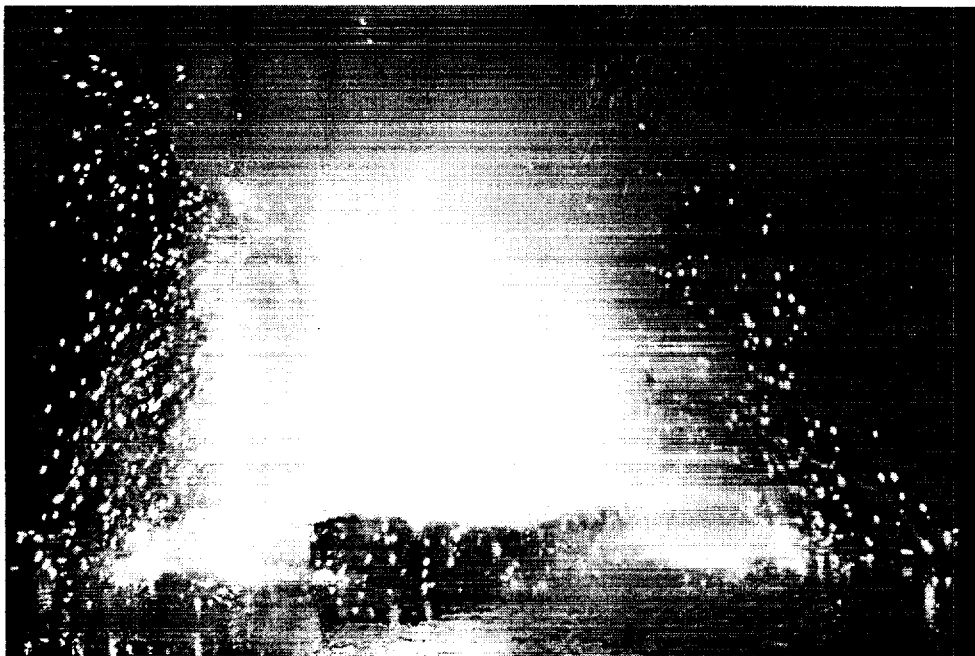
Figure 2. Magnesium fire during suppression with liquid agent.